Appl. Ser. No. 10/765,246
Attorney Docket No. 11460-130
Appendix A



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RULE 132 DECLARATION

The undersigned, Jerald P. Dykstra, states:

1. I am Director of Intellectual Properties at Epion Corporation, Billerica, Massachusetts ("Epion"), assignee of the instant U.S. Patent Application Serial No. 10/765,246. I have been affiliated with Epion for over five (5) years and through that employment, and previous employment and education over the course of twenty-five (25) years, have been involved with design, development of, manufacturing of, and intellectual properties for ion beam processing equipment and ion beam processing methods, including ion implanters and ion implantation and gas cluster ion processing and equipment. I am familiar with Epion developments in materials modification including methods and apparatus for gas cluster ion beam production and use, ion implantation, ion beam assisted vapor deposition and the like.

2. I have studied and am familiar with the above-identified application's specification and claims, as well as the Office Action dated May 4, 2005 concerning the application, and the two patents cited as prior art in the Office Action, U.S. Patent Nos. 6,770,874 to Dykstra (the '874 patent), and 6,831,272 to Mack et al. (the '272 patent.) I am, in fact, the sole inventor of the '874 patent.

3. At the time that the claimed invention was made, and at all times subsequent thereto, the subject matter of the '874 patent and the '272 patent was and is owned by or subject to an obligation of assignment to Epion (or its corporate predecessor of the same name.)

4. There have been no publications describing, offers for sale, or public uses of products or processes embodying the subject matter of the '874 or '272 patents pre-

dating the January 27, 2003 filing date of U.S. Provisional Patent Application Serial No. 60/442,854 to which the present application claims priority.

5. The work of David R. Swenson, inventor of the subject matter of the instant application, was known to me and the inventors of the '272 patent, Michael E. Mack and Richard P. Torti, and vice-versa. Submitted with the response to the instant Office Action is a paper authored by Mr. Swenson entitled "Measurement of averages of charge, energy and mass of large, multiply charged cluster ions colliding with atoms", Nucl. Instr. & Meth. -B (the Swenson paper.) The Swenson paper was first published on the Internet March 18, 2004, after the respective filing dates of the instant application and the provisional application to which it claims priority. The Swenson paper acknowledges discussions with Messrs. Mack and Torti regarding "existing methods" and the "need for" more comprehensive measurements. Swenson has devised better methods and apparatus for more useful measurements than provided by time-of-flight (TOF) techniques alone.

6. Both the instant application (starting at par. [0006]) and the Swenson paper explain the motivation for the presently claimed invention, and the inadequacies of simple TOF techniques as disclosed in the '674 and '272 patents. Specifically, lines 99-110 of the Swenson paper speak to the novelty of the presently claimed invention relative to such simple TOF measurement techniques. Had the presently claimed invention been an obvious extension of existing TOF measurement techniques, it would not have merited publication in the peer-reviewed journal, Nuclear Instrumentation and Methods in Physics Research B.

7. I find Swenson's work to be a beneficial addition to the state of the art. The apparatus and techniques of the presently claimed invention have enabled the measurement of the data in Table 1 and Figure 3 of the Swenson paper. These measurements led to an understanding of the transformation of gas cluster ion beam (GCIB) cluster ions traversing a pressurized gas cell, and the development of technology

that is offered for sale with each commercial Epion GCIB processing tool. The presently claimed invention has enabled new measurements that led to new understanding and subsequent incorporation of the pressurized gas cell into the commercial GCIB processing product.

8. The Office Action asserts that the '874 patent "discloses methods and equations for measurements of various parameters of cluster ions in a cluster ion beam." While this is true, the "various parameters" disclosed are limited to: (a) the cluster size or mass (N or $m_i$) and/or the distribution of the cluster size or mass (N or $m_i$), but only for the special case of cluster charge state q =1; and (b) in the more general case where q is unknown, only the parameter N' and/or its distribution, N' being the ratio cluster mass N to the unknown charge state q. Further, the '874 patent states "at present there is no easy separation of these distributions" and, referring to N', "this generalization somewhat reduces the utility of the measurement". Such measurements are only precise when q = 1 or it has been arranged that q is very approximately 1. N' is a useful parameter for beam and process control, but it is not a substitute for the actual charge state q or charge distribution or the actual average charge $\overline{q}$ of the clusters. The parameter N' cannot distinguish between clusters of 1000 atoms having a single charge and clusters of 10,000 atoms having a charge state of 10. This is exactly the problem described in the NIM-B paper lines 96 – 110. This is exactly the problem stated in the instant application (at par. [0007] following equation 1.) The '874 patent does not disclose how to measure the average energy $\overline{E}$ nor the average mass $\overline{m}$ nor the average charge state $\overline{q}$ of the clusters when the charge state q of the clusters is unknown.

9. The Office Action also states "By using equations 1-3, the ratio of electric current to particle flow yields the cluster charge and....." I respectfully indicate that this assertion is in error, one that illustrates an important difference between the presently claimed invention and the prior art. The referenced statement indicates the belief that equations 1-3 can yield a cluster particle flow measurement, and that by combining that with a current measurement using a Faraday enclosure, the average cluster charge can be

calculated. In fact, a cluster particle flow rate cannot be determined from equations or other teachings in the '874 patent. The current measurement disclosed in the '874 patent can be used (in the general case of unknown charge states q) to determine $N' = N/q$, but the total number $N_C$ of clusters flowing or arriving in a unit of time cannot be determined and thus an average charge per cluster $\overline{q}$ cannot be determined. The present invention addresses this problem by using a beam attenuator to create a sample of the beam, reducing the cluster flow or arrival rate to a level at which the individual cluster arrivals can be counted as discrete events, enabling an independent measurement of cluster flow or arrival rate.

10. The Office Action includes an assertion "...and their various ratios can readily be converted to their average values, for example, by simply repeating the measurements and taking their averages." However, the averages $\overline{q}$, $\overline{E}$, and $\overline{m}$ are averages across populations of cluster ions, not over time – they cannot be determined by repeating (in time) the measurement and averaging.

11. The Office Action states that the '874 patent discloses "...providing a cluster ion beam attenuator (120 in Fig.3)..." Item 120 in Fig 3 in '874 is a gas skimmer aperture 120 that separates gas products that have not been formed into a cluster jet from the cluster jet so as to minimize pressure in the downstream region (col. 4, lines 44-47). The skimmer has no purpose or intent to "attenuate" a beam, but rather is intended to fully transmit the cluster jet while blocking flow of gas that has not been incorporated into the jet by the nozzle. In the present application, Figure 2 discloses as prior art the same skimmer 120 and paragraph [0029] describes it identically. In the present application, Fig. 3A and other figures show beam attenuator 302 and attenuator aperture 303 (par. [0035]) having a purpose of reducing the cluster flow rate within the beam to an accurately countable rate (par. [0040].) It is respectfully submitted that in the present application, Figures 9-11 show both the skimmer 120 and the attenuator 302, clearly indicating that these components are distinct and therefore it is an improper reading of the '874 patent to assert that the skimmer is equivalent to the "attenuator" of the present

invention. The use of an "attenuator" to permit accurate measurement of particle flow by direct individual counting of particles using a photomultiplier tube or other sensor is a novel feature of the presently claimed invention.

12. The instant Office Action seems to ascribe to the disclosure of the '272 patent "... cluster ion beam current measurement means for measuring a current of the attenuated sample of the gas cluster ion beam ..." and later "...particle flow rate measurement means for measuring a particle flow rate of said attenuated sample ..." Similarly, the '272 patent discloses no beam attenuator, but only a skimmer 120 (Figure 2) identical to that of the '874 patent and the present invention. Mack does disclose a beam gating device 212 having open and closed states that controllably shuts off or restores the beam creating a transient for TOF measurement, however that element is not an attenuator either.

13. Finally, the instant Office Action states " ... means for measuring an average energy per charge, $\left(\frac{E}{q}\right)_{average}$, of the cluster ions in the attenuated sample of the cluster ion beam; calculating means for processing measurements of $\left(\frac{E}{q}\right)_{average}$, flow rate, beam current and average velocity, to calculate a measure of an average mass of cluster ions in the GCIB..." Mack does not disclose $\left(\frac{E}{q}\right)_{average}$ measurement. The only measurement described in Mack is the measurement of the transient of current in the Faraday when the beam is gated on or off. From that current measurement, a calculation determines a cluster size distribution f(n) and/or mass distribution, and only for the special case where the charge state of the beam is known or can be assumed to be $q = 1$. When the charge state is non-uniform from cluster to cluster, the calculation only determines the distribution f(n/q), which is less useful.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United State Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: November 4, 2005

By: Jerald P. Dykstra
Jerald P. Dykstra

11460-130_Rule132_110405

# JERALD P. DYKSTRA

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## EXPERIENCE

**Epion Corp.,** **2000 to Present**
Billerica, MA

Jan., 2000 – Present Director of Intellectual Properties
(w/responsibility for all intellectual property activities of the corporation in the fields of equipment and processes for ion implantation, film deposition, and gas cluster ion beam systems.) Also includes (as inventor) one patent in the field of gas cluster ion beam processing of semiconductor materials – other patents pending.

**Independent Consultant** **1999**
J. Dykstra, Consulting
Austin, TX

Consulting services in the field of intellectual properties for ion beam equipment and processes.

**Eaton Corp.,** **1977 to Dec.**
**1998**
Semiconductor Equipment Operations
Austin, TX (HQ Beverly, MA)

Six patents in the fields of ion implanter controls and ion implanter system designs. From 1980 to 1996, managed all aspects of the plant's patent, copyright, trademark, and trade secrets activities. From 1996 to 1998, responsibilities extended to all plants in Eaton's worldwide Semiconductor Equipment Operations (SEO) including considerable US — Japan coordination. From 1990 to 1995, chaired SEO's Joint Technology Advisory Group which coordinated joint developments and technology transfers between SEO's US and Japanese plants, for all ion implantation equipment products.

| | |
|---|---|
| July, 1996 — Dec. 1998 | Director, Intellectual Properties (w/responsibility for semiconductor equipment intellectual property activities in Austin TX, Beverly MA, Rockville, MD, and Toyo, Japan plants) |
| Jan., 1995 — July, 1996 | Plant Manager (Austin Plant ~ 400 employees - managed all medium current ion implantation product activities, including manufacturing, engineering, marketing, and service) |
| Apr., 1986 — Jan., 1995 | Director of Engineering ( ~ 80 employees — developed 4 generations of world-class ion implanter equipment — managed all R&D, development, engineering, application, and intellectual properties activities) |

**Eaton Corp.,** (continued)

| | |
|---|---|
| Apr., 1984 — Apr., 1986 | Engineering Manager, (ion implantation equipment and process development) |
| Nov., 1980 — Apr., 1984 | Sr. Project Engineer, (ion implantation equipment development) |
| Nov., 1979 — Nov., 1980 | Project Engineer, (ion implantation equipment development) |
| Nov., 1977 — Nov., 1979 equipment | Sr. Electronic Design Engineer, (ion implantation development) |

**AMSCO Medical Electronics/Medical Monitor Systems** **1973 to 1977**
Austin, TX

Six patents in the field of medical instrumentation for patient data measurement and acquisition. Managed all aspects of the company's engineering and development activities, including patent and trademark activities.

| | |
|---|---|
| May, 1973 — Nov., 1977 | Chief Engineer ( managing ~ 20 employees) |
| May, 1971 — May, 1973 | Project Engineer |
| May, 1969 — May, 1971 | Design Engineer |

## EDUCATION

BSEE – Honors – biomedical, electronics, & physics (Univ. of Texas at Austin, Jan., 1969)
MSE — (Univ. of Texas at Austin, Jan., 1975)

## SKILLS

Broad interest in and understanding of technology, especially in the fields of Atomic Physics, Nuclear Physics, Radiation Effects and Safety, Vacuum Systems, High Voltage Technology, Astronomy, Electronics, Computer Hardware, Software, Biomedicine, Physiology, Genetics, Semiconductor Fabrication, Robotic Automation, Clean-room Technology, Ion Sources, and Beam Optics.
Rare combination of skills in management, technology and intellectual properties.

## ADDITIONAL INFORMATION

**Journal Publications**

1. J. Dykstra, A. Arrale, and M. Schneider, "Process and equipment considerations in the implantation of GaAs", *ION IMPLANTATION TECHNOLOGY-98* (Proceedings of 12$^{th}$ Intl. Conf. on Ion Implantation Technology, Kyoto, Japan, June, 1998) 71-74.
2. K. Saadatmand, E. McIntyre, S. Roberge, Z. Wan, K. Wenzel, R. Rathmell, and J. Dykstra, "Radiation Safety Study for Ion Implanters when Implanting Hydrogen and Deuterium", *ION IMPLANTATION TECHNOLOGY-98* (Proceedings of 12$^{th}$ Intl. Conf. on Ion Implantation Technology, Kyoto, Japan, June, 1998) 292-295.
3. A.Ray, J. Dykstra, & R. Simonton, "Overview of the Eaton NV-8200P high beam purity, parallel scanning implanter", *ION IMPLANTATION TECHNOLOGY-92* (Proceedings 9$^{th}$ Intl. Conf. on Ion Implantation Technology, Gainesville, FL, 1992)
4. A. Ray & J. Dykstra, "Beam incidence variations in spinning disk ion implanters", *Nucl. Instr. & Meth. in Physics Research* B55 (1991) 448-492.
5. J. Dykstra, A. Ray, & Robert Simonton, "A versatile ion implanter for planar and 3D device construction", *Nucl. Instr. & Meth. in Physics Research* B55 (1991) 478-481
6. J. Dykstra, A. Ray & R. Simonton, "NV-6200AV: A versatile ion implanter for submicron and 3-D device engineering", *SPIE Vol. 1405* (Fifth Congress of the Brazilian Society of Microelectronics (1990) Sao Paulo, Brazil)

7. S. Sampayan, M. King, L. Frisa, R. Moore, & J. Dykstra, "Enhanced ionization Freeman ion source", *Nucl. Instr. & Meth. in Physics Research* B37/38 (1989) 90-93
8. J. Fleming, J. Dykstra, M. King, A. Ray, & R. Simonton, "NV-6208: A midcurrent ion implanter with constant beam angle of incidence", *Nucl. Instr. & Meth. in Physics Research* B37/38 (1989) 601-604

**US patents** (most have foreign counterparts)

| | |
|---|---|
| D 246,352 | Probe cover (for a medical device) |
| 3,884,219 | System for determining temperature and respiration rate (medical instrument) |
| 3,940,742 | Data acquisition, storage and display system (medical instrument) |
| 4,053,951 | Data acquisition, storage and display system (medical instrument) |
| 4,116,228 | Respiration data acquisition, conversion and display system (medical instrument) |
| 4,125,111 | Heartbeat data acquisition conversion and display system (medical instrument) |
| 4,514,637 | Atomic mass measurement system (ion implantation) |
| 4,700,077 | Ion beam implanter control system (ion implantation) |
| 4,929,840 | Wafer rotation control for an ion implanter (ion implantation) |
| 4,943,728 | Beam pattern control system for an ion implanter (ion implantation) |
| 5,091,655 | Reduced path ion beam implanter (ion implantation) |
| 5,177,366 | Ion beam implanter for providing cross plane focusing (ion implantation) |
| 6,331,227 | Enhanced Etching/Smoothing of Dielectric Surfaces (gas cluster ion processing system) |
| 6,624,081 | Enhanced Etching/Smoothing of Dielectric Surfaces (gas cluster ion processing) |

Additional patents pending

**Technical / Industry Conference and Seminar Participation**

1998 "XII Intl. Conf. on Ion Implantation Technology — 98", Kyoto, Japan — 5 days
1997 "Ion Implantation Conference — ICON'97", Scottsdale, Ariz. — 4 days
1996 "XI Intl. Conf. on Ion Implantation Technology — 96", Austin, TX — 6 days
1994 "X Intl. Conf. on Ion Implantation Technology — 94", Catania, Italy — 5 days
1993 "ISSM '93 Int'l. Symp. on Semiconductor Manufacturing,", Austin, TX — 2 days
1992 "IX Intl. Conf. on Ion Implantation Technology — 92", Gainsville, FL — 4 days
1990 "Application of Accelerators in Research and Industry — 90", Denton, TX — 3 days
1990 "VIII Intl. Conf. on Ion Implantation Technology — 90", Guildford, UK — 5 days
1990 "Fifth Congress of the Brazilian Society of Microelectronics", Sao Paulo, Brazil — 3 days
1988 "Int'l Workshop on Physics of Semiconductor Devices — 89", New Delhi, India — 3 days
1988 "VII Intl. Conf. on Ion Implantation Technology — 88", Kyoto, Japan — 4 days
1986 "VI Intl. Conf. on Ion Implantation Technology — 86", Berkeley, CA — 5 days
1984 "V Intl. Conf. on Ion Implantation Technology — 84", Smugglers Notch, VT — 5 days

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# Measurement of averages of charge, energy and mass of large, multiply charged cluster ions colliding with atoms

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**Abstract**

A new technique is described that has allowed the first measurements of the averages of charge, energy and mass of large, multiply charged, gas clusters. The technique is used to investigate cluster–gas collisions. For this study, a beam with averages of charge state +3.2, energy 64 keV and mass 10,400 atoms was produced in a state-of-the-art high intensity Ar gas cluster ion beam, and the stability of these clusters undergoing collisions with Ar gas atoms was measured using a gas cell target. With a target thickness of $2.2\times10^{14}$ atoms/cm$^2$, the cluster mass and energy are reduced to 0.22 of the original values while charge is less affected and the velocity is nearly constant.


*PACS:* 36.40.Wa; 39.90.+d; 36.40.Qv; 34.90.+q
*Keywords:* Cluster charge; Cluster–atom collisions; Cluster energy; Cluster mass

## 1. Introduction

This paper reports the first measurements of charge state $q$, energy $E$ and mass $m$ for large gas cluster ions. These clusters are aggregations of atoms that are formed through condensation and coagulation of a gas in a supersonic flow [1,2]. Typically the resulting jet of clusters is ionized using electron impacts and is accelerated to form a charged particle beam. Study of these ions has been limited because $q$, $E$ and $m$ could only be inferred for very small clusters using conventional instrumentation. For example, instruments based on accelerations in electric and magnetic fields yield only the $m/q$ or $E/q$ ratios (J.J. Thompson's measurement of $m/q$ of the electron in the year 1898 is a good example). For most ionized particles this is not a problem because either $m$ or $q$ is already known. For multiply charged particles, one can infer the charge state by looking for associated peaks of the same mass but different charge if they can be resolved. For clusters this is not always possible because the spectrum is broad and complex, and spectrometer resolution is limited (the clusters studied in this paper have the same momentum as a 3.1-GeV proton). A further complication is caused by the small binding energy (≈90 meV for an Ar atom in a cluster); ionization and other processes can radically alter the mass of the cluster through evaporation, fragmentation, or even "coulomb explosion". Conventional tech-

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niques have allowed $q$, $E$ and $m$ to be determined only for clusters with $m/q < 200$ atoms [3–5]. [1] For larger, multiply charged cluster ions the mass and charge are ambiguous, and without this knowledge it is not possible to understand the basic physics that determine their stability and the nature of the collisions they make with other particles or surfaces. Understanding the $q$, $E$ and $m$ of large clusters is of intrinsic interest and has important applications because gas cluster ion beams (GCIB) is a rapidly emerging technology used for smoothing, cleaning and etching surfaces, in depositing coatings or doping materials, and for other industrial uses [6–14].

Using GCIB to smooth or etch a surface has motivated this work and illustrates a particular need to understand $q$, $E$ and $m$ for large clusters. The surface modifications are the result of individual cluster impacts that move and eject material by direct sputtering and through melting and evaporation; with each cluster creating a crater of specific depth and diameter. These craters, on the scale of 10 nm [15], are remarkably analogous to craters on the scale of 100 km made by meteorite impact on planetary bodies; in both cases the projectile velocity is of the order of 10 km/s. Predicting the characteristics of the craters requires knowledge of the mass and impact velocity of the object. Cluster velocity can be measured using TOF, and, historically, cluster mass was determined by using singly charged clusters and conventional measurements. But our recent efforts to increase the intensity of GCIB beams are producing more highly charged clusters. If the clusters remain intact after ionization, their charge state distribution would be determined by Poisson statistics [16]. For example, the average $q$ of a beam undergoing random, successive, singly ionizing, electron impacts would be 3 if 95% of the clusters were ionized. Thus a highly ionized cluster beam could also be a multiply charged beam. With the same acceleration potential, the higher-charged clusters will make larger craters and decrease the ultimate smoothness of a GCIB-processed surface but should increase etch rates. When the electrical current of the beam is used for dosimetry, higher-charged clusters will produce fewer but larger craters than a lower charged beam for equal doses. To give added perspective to this work, we have found using TOF measurements that the average $m/q$ of our Ar GCIB changes from 30,000 to 1000 atoms/charge as the current of ionizing electrons is increased. Using existing techniques it was not possible to know whether they had become 30,000 atom clusters with +30 charges or whether they had fragmented such that they were 1000 atom, singly charged clusters or some intermediate value of mass and charge. The new method described next was required to determine for the first time the averages of $q$, $E$ and $m$ for these large clusters, and particularly whether the clusters were highly charged; and it has allowed a first view of the abrasion process that occurs when large, high-energy cluster ions pass through a gas.

## 2. Technique

The beams were produced by a commercial GCIB processing machine [2] described in detail in [16]. A jet of clusters is produced as high-pressure (7.6 bar) Ar gas expands adiabatically in supersonic flow into vacuum. [3] The jet passes through a conical skimming aperture that selects the core of the jet where the cluster intensity is greatest. [4] The clusters are then ionized by electron impact and electrostatically accelerated with a maximum po-

[1] Other methods have been used to determine $q$, $E$ and $m$ for very-large very-highly charged ($q > 1000$) molecules produced by electrospray techniques, and also for the case of highly charged atoms in the solar wind or electrostatically accelerated dust particles. These techniques are not applicable to GCIB beams because, for the former case, the charge states are too low, and with the latter technique, because the cluster's collision energy is deposited nearly all thermally and hence cannot be detected using known methods. There are other techniques for measuring the size of uncharged clusters in the thermal jet before they are ionized and accelerated.

[2] Epion Corporation model Ultra-Smoother® 200 GCIB surface processing system that was modified to include QEM measurements.

[3] Using a conical nozzle with 50-μm diameter orifice.

[4] For these experiments the skimmer diameter was 0.5 mm and the nozzle-to-skimmer distance was 37 mm.

tential of 30 keV. Next, a dipole magnet deflects monomers and dimers out of the beam. [5] The beam passes through a cylindrical cell with a pressure gauge where variable target thicknesses of Ar gas are introduced to measure the effect of cluster–gas collisions. The beam continues on to the charge, energy and mass (QEM) detection apparatus described next.

The QEM measurement technique consists of making three separate measurements of average energy per charge $\{E/q\}_{\text{ave}}$, average velocity $\bar{v}$ and $\bar{q}$, on a sample of an ion beam. The $\{E/q\}_{\text{ave}}$ is measured using an electrostatic spectrometer, and the velocity is measured using TOF, both of which are familiar techniques. What is unique to this method is the measurement of $\bar{q}$ and its use in combination with the other measurements to determine $\bar{m}$ and $\overline{E}$ for the cluster distribution. The average charge is measured by alternately measuring the flow rate of particles $\Gamma$ using a fast particle counter and the electrical current $I$ using a Faraday cup for a small sample of an ion beam. The average charge state of the cluster sample is: $\bar{q} = I/(e\alpha\Gamma)$, where $\alpha$ is the relative detection efficiency. This measurement is then combined with the electrostatic spectrometer measurement to determine the average cluster energy: $\overline{E} = \bar{q}\{E/q\}_{\text{ave}}$, and then with the TOF measurement to give: $\bar{m} = 2\overline{E}/\bar{v}^2$. Alternatively a measurement of $m/q$ can be used giving $\bar{m}$ as: $\bar{m} = \bar{q}\{m/q\}_{\text{ave}}$. [6] Each of these equations is strictly valid if the particular distributed quantities (which are represented by mean values) are uncorrelated. As this is the first use of this technique, the degree of correlation is presently unknown and will need further study. [7] The correlations are expected to be weak because the collisional processes that change $m$ or $q$ have cross sections that scale as $m^{2/3}$ and because of their stochastic nature. [8] Numerical simulations have been used to test these assumptions as discussed later. A future version of the apparatus is planned that will measure the distributions directly and this will be the topic of future papers.

Fig. 1 shows the particular QEM apparatus used but many variations of the measurements and detectors are possible. The apparatus consists of an attenuator, then an electrostatic spectrometer, followed by a particle detector. The attenuator is two successive small pinhole apertures that select a small fraction of the phase space of the beam resulting in a highly collimated beamlet that is attenuated by a factor of $10^6$ or greater. The electrostatic spectrometer deflects the beam through a resolving aperture and into an electrostatically suppressed Faraday cup to measure the $E/q$ spectrum of the beam. The spectrum is integrated to obtain $I$. With the spectrometer powered off, the beam passes through a hole in the spectrometer electrode and into the particle detector. This allows the electrostatic spectrometer to function as an electrostatic gate for the beam, deflecting charged clusters so that energetic neutral clusters can be detected. The particle detector is similar to the Daly detector [17] but with the particles striking at an angle from the normal to increase secondary-emission yield, and to allow extraction of the secondary electrons without the need for a magnetic field. The negatively biased dynode adds energy to the clusters and accelerates the secondary electrons. The secondary electrons pass through two highly transparent screens and a

[5] The GCIB source produces a co-propagating monomer beam that was removed to assure that only the cluster distribution was included in the averages of $q$, $E$ and $m$. The large emittance of the beam caused the small dispersion produced by this magnet to have a negligible affect on the cluster measurements.

[6] Similar values of $\bar{m}$ were obtained using a pressure-gauge-equipped Faraday cup to measure $m/q$. However, this method is less desirable because the pressure gauge measurement averages the spatial distribution, where as $\bar{q}$ is measured at one position in the beam.

[7] The natures of the distributions are unknown. The $m$ distribution begins as lognormal, the $q(m)$ distribution would be Poisson if the clusters remain intact but there is strong evidence that the ionization process alters the $m$ and $q$ distributions and hence $v(E,m)$ is also unknown. If the cluster $m$ and $q$ remain constant during and after acceleration then $E/q$ is a constant and the determination of $E$ is strictly valid, but as will be seen, this is not always a good approximation.

[8] This assumes that the collision cross sections are $\pi r^2$ where $r$ is the cluster radius which scales as $m^{1/3}$.

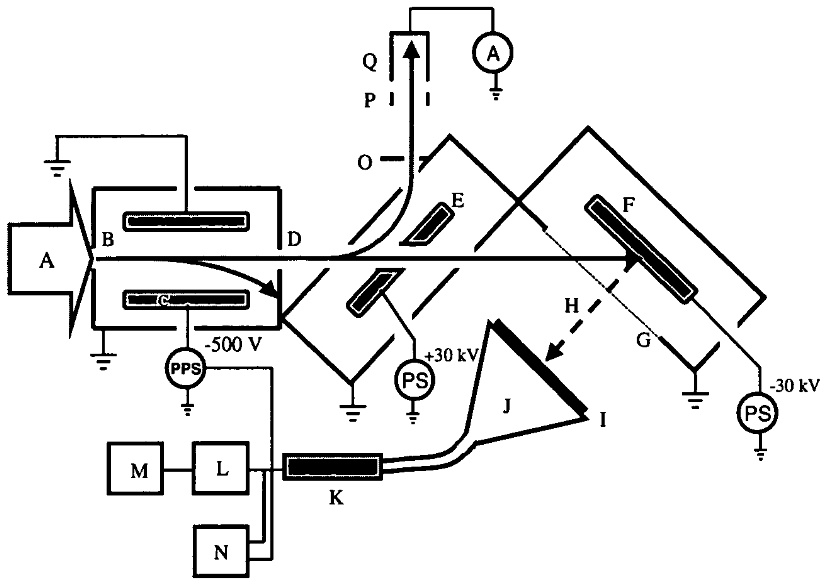


Fig. 1. Schematic diagram of apparatus with particle trajectories. The parts are as follows: (A) cluster ion beam, (B) sampling aperture, (C) TOF deflection electrode connected to pulsed power supply, (D) aperture, (E) electrostatic spectrometer electrode, (F) dynode, (G) high-transparency screen, (H) secondary emission electrons, (I) aluminized-Mylar film and scintillator, (J) light guide, (K) PMT, (L), pulse discriminator, (M) pulse counter, (N) oscilloscope, (O) resolving aperture, (P) suppression electrode, (Q) Faraday cup.

thin aluminized-Mylar film to strike a scintillator, producing photon pulses that are detected by a fast photo-multiplier-tube (PMT). The particle pulse rate was measured using either a pulse-discriminator-counter system, or by digitizing the PMT anode current with a fast digital oscilloscope. [9] With the latter system, software was used to analyze the waveform, detecting the peaks and their heights, and generating a pulse height spectrum of which Fig. 2 is an example. The dynode was biased at −30 kV so that clusters struck the dynode with a maximum of 60 keV/$q$ and the secondary electrons deposited 30 keV in the plastic scintillator, producing, on average, 300 photons per electron. The photons are transported through a light guide to the PMT located outside the vacuum chamber. The maximum count rate of the PMT-discriminator-counter system was 100 MHz which, if the clusters were singly charged, would correspond to 16 pA of current; thus the beam was greatly attenuated for the measurements. [10] The particle detector is also used for the TOF measurement because of its sensitivity and fast time response. For the TOF measurement, a transverse electrostatic deflector between the apertures of the attenuator is used as a fast switch to gate the beam on and off, and the time dependant particle signal is detected directly as the PMT anode current, averaged, and then recorded using an oscilloscope. [11] It should be noted that all of these separate measurements require that the signals remain constant over time periods long enough to complete them, as was the case in these experiments. [12]

Obtaining absolute values of $\bar{m}$, $\bar{q}$ and $\bar{E}$ requires calibration of the detectors. The electrical

[9] Agilent Technologies 54832D, 4 giga-sample/s.

[10] When the QEM is used for characterizing a GCIB beam, a slit or array of apertures is used to sample the beam at multiple locations.

[11] The TOF distance was 272 mm.

[12] The first measurements that are presented were measured over several days. With refinement, measurements have been completed in less than one day.

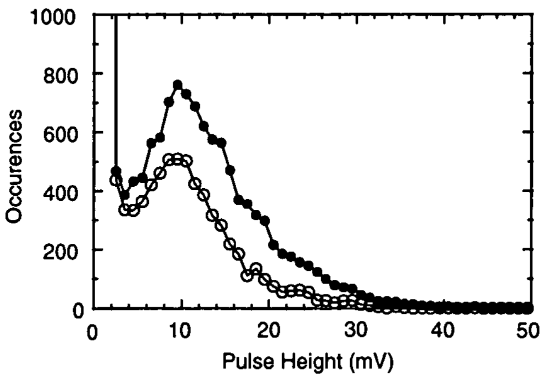


Fig. 2. Histogram of PMT pulse heights for ionizer conditions such that $\bar{q} = 1.0$ (○), and $\bar{q} = 4.0$ (●).

current signal of the attenuated beam was large enough to be measured by NIST traceable pico-ammeters. The electrostatic spectrometer was calibrated using the spectra of monomer beams (the monomer deflection magnet was removed) because $E/q$ is known and the small energy spread allows a precise determination of the energy-acceptance-width. The detection efficiency of the spectrometer and Faraday cup was found to be 0.96 by comparing $I$ to a second Faraday cup that measured the undeflected beam current. [13] The detection efficiency of the particle detector depends on: the secondary electron emission yield from the dynode, the scintillator photon yield, transmission probabilities for the electrons and photons, the detection efficiency and gain of the PMT and the pulse discriminator setting. This efficiency was measured using a singly charged Ar GCIB. For this comparison the beam attenuation was reduced and the ionizer was run at low power such that the probability of multi-charging the clusters was low. A value of $\alpha = 0.7$ was determined for large clusters (30,000 atoms), with velocity of 2 km/s, verifying that more than one secondary electron is produced in each cluster-dynode impact even for these slow, singly charged clusters. [14] Also the beam acceleration voltage was not a significant effect in the range of 10–30 kV under these conditions. The typical peak height distribution shown in Fig. 2 indicates that nearly all of the clusters are resolved. [15] The background for the particle detector was measured by interrupting the beam with a mechanical beam block, and was negligible. The background for the current measurement was minimized by carefully shielding the cables and by passive filtering of high-frequency noise.

## 3. Results and discussion

The stability of Ar clusters accelerated with 30 kV and then colliding with Ar gas was studied using the gas cell and the QEM detector. The initial cluster size was 10,400 atoms, which is much larger than in any previous cluster–atom collision experiment. [18–25] Table 1 summarizes the QEM measurements for the various target thickness. From the electrostatic spectrometer data, graphed in Fig. 3(a), it can be seen that measured $E/q$ is always less than 30 keV/$q$ and decreases rapidly with increasing target thickness. The average charge decreases more slowly than the average energy, while the TOF data shows that cluster velocity is nearly constant. The resulting QEM

[13] The second Faraday cup replaced the dynode.

[14] The particle rate $\Gamma$ did not fully saturate with increasing dynode voltage nor was the signal completely separated from the noise as shown in Fig. 2, therefore $\alpha$ was a function of dynode voltage, the conditioning of the native oxide surface of the Al dynode; and of the PMT gain, deadtime correction and discriminator settings. The systematic error of $\bar{q}$ caused by $\alpha \neq 1$ is much less than 0.30 because both the normalization measurement and the data were measured using the same dynode voltages, PMT settings, and had similar count rates, pulse heights, and dynode conditions. The normalization procedure also corrects for drifts in the calibrations of the pico-ammeters and after pulsing of the PMT, which may also have contributed to $\alpha < 1$. The current $I$ was read by two different pico-ammeters with a relative error of 0.14.

[15] The data in Table 1 were measured using the discriminator and counter method. The pulse high distribution was used to confirm the PMT gain/discriminator settings. The lack of complete resolution of the cluster distribution was corrected by measuring $\alpha$.

Table 1
Experimental measurements using gas cell and derived quantities $\bar{q}$, energy $\overline{E}$ and mass $\bar{m}$

| Thickness (atoms/cm$^2$) | $\Gamma$ (MHz) | $I/e$ (MHz) | $(E/q)_{\text{ave}}$ (keV/$q$) | $V$ (km/s) | $\bar{q}$ | $\overline{E}$ (keV) | $\bar{m}$ (atoms) |
|---|---|---|---|---|---|---|---|
| 1.7E+13 | 39 | 86 | 20.4 | 5.5 | 3.2 | 64.5 | 10,400 |
| 5.3E+13 | 45 | 83 | 16.8 | 5.6 | 2.6 | 43.7 | 6710 |
| 8.8E+13 | 40 | 76 | 14.7 | 5.7 | 2.7 | 40.2 | 6000 |
| 1.2E+14 | 46 | 88 | 11.3 | 5.6 | 2.8 | 31.2 | 4810 |
| 1.5E+14 | 47 | 96 | 9.8 | 5.5 | 2.9 | 28.7 | 4600 |
| 1.8E+14 | 42 | 49 | 10.7 | 5.4 | 1.7 | 18.1 | 2990 |
| 2.1E+14 | 36 | 39 | 9.1 | 5.3 | 1.5 | 13.8 | 2360 |

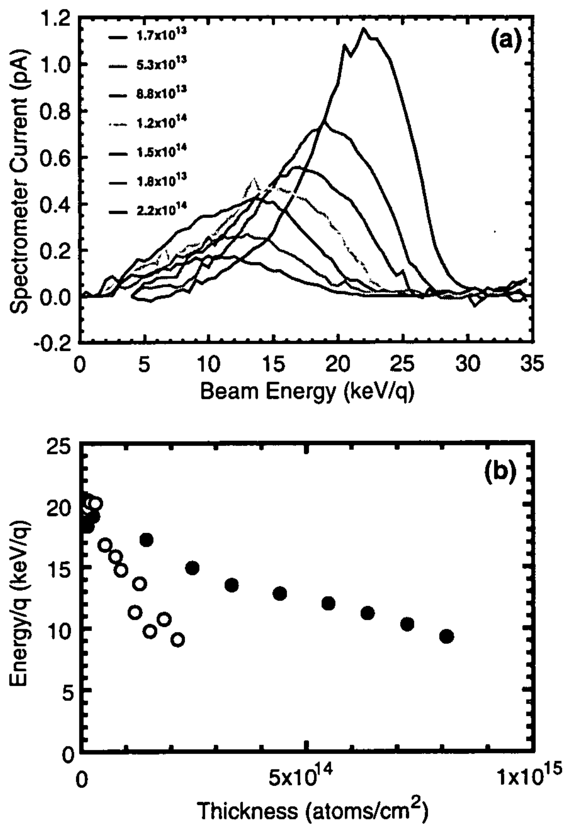


Fig. 3. (a) Faraday current as a function of spectrometer $E/q$ setting for various target thickness (atoms/cm$^2$). (b) $(E/q)_{\text{ave}}$ as a function of target thickness for two ionizer conditions: (O) $\bar{q} = 1$, (●) $\bar{q} = 3$ (calculated for data of (a)), with $\bar{q}$ determined at the lowest thickness.

values show that the clusters are slowly abraded by multiple gas collisions with the cluster $\overline{E}$ and $\bar{m}$ most affected. The data was fit to a Monte-Carlo simulation that assumed: a lognormal initial mass distribution, collision cross sections equal to $\pi r^2$ where $r$ is the cluster radius [26,27], mass loss equal to the ratio of impact energy to binding energy per atom for each gas–cluster collisions. With these assumptions, the clusters initially lose an average of 130 atoms in a collision with an Ar atom. The model also allows the effects of correlations in the distribution to be studied. These caused a relative error in $\bar{m}$ of less than 0.05, but for $\overline{E}$ the error grew from 0.05 in the absence of gas collisions to +0.40 for the thickest target. [16] The QEM data show that cluster charge decreases more slowly than the cluster mass, and clusters with increased $[E/q]$ or $[m/q]$ were not detected in the spectra. These three observations all indicate that cluster charge is much more tightly bound than the mass of the cluster. Fig. 3(b) is a plot of $[E/q]_{\text{ave}}$ at different gas-target thicknesses for the clusters of Fig. 3(a) and for lower charged clusters. It shows that lower charged clusters are less affected by the gas collisions and that loss processes other than collisions in the gas cell are significant. The energetic neutral fraction of the beam was also studied. Even at the highest target thickness the neutral cluster content of the beam appeared to be less than 0.05. However, the detection efficiency of neutral clusters has not been determined, and further study will reveal whether neutral clusters are not present, or whether lack of coulomb potential energy causes the secondary electron yield to be too low for detection [28–30].

[16] These results will be reported more fully in a later publication.

## 4. Conclusions

While there is more to learn about the QEM technique, in particular why $\alpha$ was not equal to one, these first results show that it can be quite accurate and reliable. The signal-to-noise is good; the quantities $\bar{q}$, $[E/q]_{\text{ave}}$ and $\bar{v}$ were measured with a one-standard-deviation relative precision of less than 0.10. The systematic errors from the particle detection efficiency, and the calibration of the ammeters are large but were corrected by measuring $\alpha$. Effects of correlations in the distributions appear to be small, except for the case of the $\overline{E}$ of highly abraded clusters. The errors of the $\bar{m}$ and $\bar{q}$ measurements are dominated by the systematic effects and are estimated to be better than 0.25 relative.

A goal of this experiment was to detect highly charged clusters, however, it has rarely detected clusters with $\bar{q}$ as great as +5 charges, even though $[m/q]$ measurements indicate that $\bar{q}$ could be as large as +30. The accuracy of the $\bar{q}$ measurements would be expected to increase with $\bar{q}$ because the larger current is easier to measure and the more energetic clusters are easier to discriminate. This paper shows that cluster–gas collisions are more abrasive for higher-charged clusters. The modeling indicates that higher-charged clusters have higher velocities and hence are much more disrupted by the gas collisions. Coulomb potential energy would also make higher-charged clusters less stable. While gas–cluster collisions may limit cluster charge, fragmentation in the ionizer before acceleration might also contribute to this unexpected result. Other effects such as electron–cluster, cluster–cluster, ion–cluster collisions and cluster stability will need to be investigated as well.

It is interesting that gas collisions cause the $m/q$ ratio to decrease. The opposite might be suspected given that coulomb forces distribute the charge near the cluster surface and repulsion favors the emission of charge. Thus the surface layers that are most likely to be abraded should have a lower $m/q$ than the cluster as a whole. But we see that gas cluster collisions do not remove charge from a cluster without first removing a disproportionately large amount of mass. This is an insight into the physics of the collisions and also into the physics of multi-charged cluster stability.

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## References

[1] E.W. Becker, K. Bier, W. Henkes, Z. Phys. 146 (1956) 333.
[2] J.M. Soler et al., Phys. Rev. Lett. 49 (1982) 1857.
[3] D. Kreisle et al., Phys. Rev. Lett. 56 (1986) 1551.
[4] M. Lezius, P. Scheier, A. Stamatovic, T.D. Märk, J. Chem. Phys. 91 (1989) 3240.
[5] W. Henkes, G. Isenberg, Int. J. Mass Spectrom. Ion Phys. 5 (1970) 249.
[6] J.-H. Song, S.N. Kwon, D.-K. Choi, W.-K. Choi, Nucl. Instr. and Meth. B 179 (2001) 568.
[7] I. Yamada, J. Matsuo, N. Toyoda, A. Kirkpatrick, Mater. Sci. Eng. R 34 (2001) 231.
[8] N. Toyoda, N. Hagiwara, J. Matsuo, I. Yamada, Nucl. Instr. and Meth. B 161–163 (2000) 980.
[9] W.K. Chu et al., Appl. Phys. Lett. 72 (1998) 246.
[10] P. von Blanckenhagen, A. Gruber, J. Gspann, Nucl. Instr. and Meth. B 122 (1997) 322.
[11] A. Gruber, J. Gspann, J. Vac. Sci. Technol. B 15 (1997) 2362.
[12] H. Hsieh, R.S. Averback, H. Sellers, C.P. Flynn, Phys. Rev. B 45 (1992) 4417.
[13] Z. Insepov, I. Yamada, Mater. Sci. Eng. A 217 (1996) 89.
[14] I. Yamada et al., J. Vac. Sci. Technol. A 14 (1996) 781.
[15] L.P. Allen et al., J. Appl. Phys. 92 (2002) 3671.
[16] M.E. Mack et al., in: Proceedings of 14th International Conference on Ion Implantation Technology, Taos, New Mexico, 2002 (IEEE, 2003).
[17] N.R. Daly, Rev. Sci. Instr. 31 (1960) 264.
[18] B. Farizon, M. Farizon, M.J. Gaillard, Int. J. Mass Spectrom. 192 (1999) 259.
[19] O. Knospe, J. Jellinek, U. Saalmann, R. Schmidt, Eur. Phys. J. D 5 (1999) 1.
[20] T. Bergen et al., Rev. Sci. Instr. 70 (1999) 3244.
[21] K. Wohrer et al., Nucl. Instr. and Meth. B 146 (1998) 29.
[22] U. Saalmann, R. Schmidt, Phys. Rev. Lett. 80 (1998) 3213.
[23] F. Ames et al., Nucl. Instr. and Meth. B 112 (1996) 64.
[24] M. Ichihashi, T. Ikegami, T. Kondow, J. Chem. Phys. 105 (1996) 8164.

[25] Z. Li, R.B. Gerber, Chem. Phys. Lett. 229 (1994) 650.
[26] F. Bottiglioni, J. Coutant, M. Fois, Phys. Rev. A 6 (1972) 1830.
[27] H. Deutsch, K. Becker, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. 114 (1995) L9.
[28] R.A. Baragiola, Nucl. Instr. and Meth. B 88 (1994) 35.
[29] J.F. Mahoney, E.S. Parilis, J. Perel, S.A. Ruatta, Nucl. Instr. and Meth. B 73 (1993) 29.
[30] R.J. Beuhler, L. Friedman, Nucl. Instr. and Meth. 170 (1980) 309.